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Energy Procedia 4 (2011) 1566–1573

Energy Procedia

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GHGT-10

# Effects of NOx in the Flue Gas Degradation of MEA

Berit Fostås[a,] 1*, Audun Gangstad[b], Bjarne Nenseter[a], Steinar Pedersen[a], Merethe Sjøvoll[a], Anne Lise Sørensen[a]

[a]*Statoil Research Centre, NO-3908 Porsgrunn, Norway*
[b]*Statoil Research Centre, NO-7005 Trondheim, Norway*

**Abstract**

Post combustion $CO_2$ capture using amine absorbents is the most mature process and therefore the most relevant choice for realising full-scale capture within the next few years. The health and environmental impact of emissions to air is, however, a potential risk. Amines may react in the process or in the atmosphere post emission to form new substances that may be more harmful than the parent amine itself.

The main objective of the current work was to investigate the flue gas degradation of monoethanolamine (MEA) in the process with special emphasis on the NOx induced chemical reactions. Degradation experiments have been carried out at absorber like conditions in the Aminox™ rig, followed by further degradation of the used solvent at higher temperature in a lab scale autoclave. Liquid samples were analysed by a range of methods to identify the formation of degradation by-products, with special focus on potential harmful compounds like nitrosamines and nitramines. On-line FT-IR and MS instruments were used for qualitative detection of volatile degradation products and to measure amine slip.

MEA is a primary amine which in itself is unable to form a stable nitrosamine. However, experiments show that under the influence of NOx, MEA degrades to the secondary amine diethanolamine (DEA) which is then nitrosated. This work shows that some nitrosamine formation in the process must be expected from any amine. Based on data from real emission measurements, health and environmental risk assessment should be investigated in further studies.



Keywords: $CO_2$-capture, Monoethanolamine (MEA); degradation; NOx

## 1. Introduction

The cost and process efficiency are widely accepted as the main criteria for selecting the best process for capturing $CO_2$ from flue gas. However, there has recently been a growing concern about possible adverse effects of

* Corresponding author. Tel.: +47-90697308; fax: +47-35564738.
*E-mail address*: bff@statoil.com.

doi:10.1016/j.egypro.2011.02.026

emissions to air on the health and environment. Theoretical studies of the atmospheric photo-oxidation of selected generic amines revealed that harmful compounds can form [1, 2]. An investigation of MEA identified formamide as the main gas phase photo-oxidation product. Formation of minor amounts of the nitramine from MEA was also reported [3]. In older studies the formation of nitrosamines and nitramines from the small alkyl-amines, dimethyl-, trimethyl-, diethyl- and triethylamine was quantified in atmospheric photo-oxidation experiments [4-6].

An obstacle to the assessment of the health and environmental risk is the almost total lack of emission data related to compounds that are of potential importance. Therefore we need to know more about the formation of potentially harmful products in the process, their emission rates and their fate in the environment. The volatile amines are especially important since they may form more harmful degradation products like nitrosamines and nitramines in the atmosphere post emission. Nitrosamines particularly represent the largest risk because they may be carcinogenic.

Three types of degradation reactions in the process are well described in the literature [7-12]. The carbamate polymerisation mechanism requires $CO_2$ and fairly high temperature. The main products are oxazolidone and higher molecular weight by-products like polyamines and cyclic amines. Oxidative degradation induced by $O_2$ produces oxidised fragments of the amine solvent and the degradation products and can thus give rise to volatile by-products. Organic acids, aldehydes, amides and ammonia are the main products from this degradation route. Heat stable salts are formed when organic acids react with the amine and will accumulate during operation. Sulphates, nitrite and nitrate salts are also formed from their presence as impurities in the flue gas. Thermal degradation is encountered at temperatures above 200$^{o}$C and is therefore not normally a significant contributor to the solvent degradation.

Until now, very few studies have been concerned with the effect of NOx in the flue gas and what by-products may form in the process as a result of the NOx induced chemical reactions. The term "NOx" represents the species NO, $NO_2$, $N_2O_3$, $N_2O_4$ and $HNO_2$. When amines are in contact with NOx-species the formation of nitrosamines and nitramines in the process must be expected. Rochelle et al. [12] suggested that nitrosamines may be formed from reactions between NO or nitrite with secondary amines or degradation products of tertiary amines. Care should also be taken to avoid degrading primary amines to secondary amines [12]. Strazisar [8] quantified nitrosamines in a degraded MEA sample by the use of a general functional group test.

It is beyond the scope of this work to conclude on what the active species in nitrosation and nitration reactions with the amines are. According to literature, only $N_2O_4$ should give rise to nitramines, whereas nitrosamines may be formed from $N_2O_3$, $N_2O_4$ and also nitrite when the reaction is catalysed by aldehydes in a basic medium. A stepwise free radical mechanism involving NO and $NO_2$ rather than $N_2O_3$ has also been suggested. Effective mass transfer and conditions at the gas-liquid interface are important to facilitate the reactions [13-16].

Based on the literature reports it seems that any amine exposed to NOx, whether it is in the process or in the atmosphere post emission, can lead to some nitrosamine and nitramine formation.

## 2. Experimental procedure

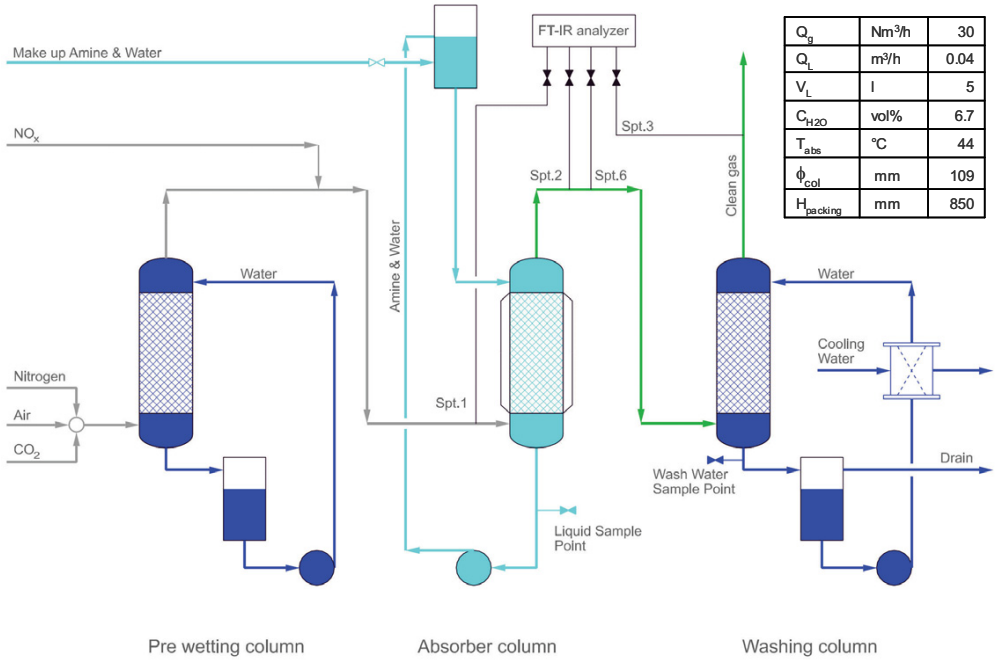
The Aminox$^{TM}$ test rig was established to study degradation reactions at absorber conditions under influence of NOx. Further degradation of the used solvent was done at stripper temperature in a bench scale autoclave. A 35 w% MEA solution has been tested.

The Aminox$^{TM}$ rig, illustrated in Figure 1 consists of a well controlled absorption column where the circulating MEA solution is counter currently contacted by a synthetic flue gas. In the random packed section of the column, a large contact area provide for good mass transfer and chemical reactions between flue gas constituents and the amine solvent. The flue gas is preheated and conditioned in the pre wetting column before it is mixed with NOx and introduced into the bottom of the absorber. The composition of the synthetic flue gas can be varied over a broad range with respect to $N_2$, $O_2$, $CO_2$, NOx and $H_2O$. $CO_2$ is absorbed by the circulating MEA during the first part of the experiment. When the amine solution is saturated with $CO_2$, the $CO_2$ supply is stopped while the concentration of the other gas components remains unchanged. Some $CO_2$ then strips off before the loading stabilizes at about 0.3 mole $CO_2$/mole MEA. The gas leaving at the top of the absorber contains traces of amine and by-products due to vapor liquid equilibrium and liquid entrainment. The gas is treated with cold water in the water wash column before it is vented. Water is condensed and amine and by-products are partly being absorbed by the circulating wash water.

Gas phase sampling points at absorber inlet and outlet and after the water wash section are connected to an on-line FT-IR analyzer so compounds in the gas can be continuously recorded. All sampling lines are electrically traced

to provide for a gas temperature of 120-150°C, condensation is thus avoided. Liquid sampling is done at intervals in selected points in the process in order to follow the amine concentration, $CO_2$ loading and the gradual increase in degradation products along with their formation. Liquid samples are analysed off line by ion chromatography, and liquid- or gas chromatography combined with mass chromatography techniques (LC-MS, GC-MS). MEA concentration and $CO_2$-loading are measured by volumetric titration.

Based on multivariate data analysis, a set of designed experiments with variation of $O_2$ and NOx concentrations at levels given in Table 1 have been performed. The NO to $NO_2$ ratio of the NOx gas was 9/1. The gas flow and the solvent circulation flow were 30 $Nm^3/h$ and 0.04 $m^3/h$, respectively. The 35 w% MEA solution was continuously exposed to the synthetic flue gas and degraded at 44°C for about 100 h in the Aminox™ test rig. The used solvent was further degraded batch wise at 120°C for 24 hours in a bench scale, stainless steel autoclave with temperature and pressure control. Liquid samples from the autoclave testing were analysed in order to detect chemical changes of solvent and degradation by-products at reaction conditions similar to the regeneration process.




| | | |
|---|---|---|
| $Q_g$ | $Nm^3/h$ | 30 |
| $Q_L$ | $m^3/h$ | 0.04 |
| $V_L$ | l | 5 |
| $C_{H2O}$ | vol% | 6.7 |
| $T_{abs}$ | °C | 44 |
| $\phi_{col}$ | mm | 109 |
| $H_{packing}$ | mm | 850 |

Figure 1 Sketch of the Aminox™ test rig for study of amine degradation at absorber conditions.

## 3. Results and discussion

Ammonia and organic acids (formic, acetic and oxalic) are the main degradation products observed in the experiments. Ammonia production is monitored by the FT-IR analyzer, and the results correspond reasonably well to earlier reported data [11]. The overall degradation rate of MEA was accelerated when NOx impurities were present in the gas, and new degradation by-products were observed.

### *3.1. Formation of nitrosodiethanolamine (NDELA)*

Results from LC-MS analyses of nitrosamines and diethanolamine (DEA) in liquid samples are given in Table 1. Nitrosodiethanolamine (NDELA) is the main nitrosamine found and it has been detected in all liquid samples exposed to NOx. The concentration increased steadily with the solvents exposure time as illustrated in Figure 2.

After 100 h degradation at absorber conditions the concentration of NDELA in MEA solution samples was in the range 10-1000 ng/g. Traces of NDELA was also detected in wash water samples from the Aminox™ rig (10 ng/g). NDELA was not detected in experiments with zero NOx nor in the fresh MEA solution. The formation rate of NDELA was considerably increased when the used solvent was heated in the autoclave, resulting in up to 40 times higher concentration of NDELA in autoclave end samples compared to Aminox™ end sampes. NDELA is non-volatile and will not tend to escape to air with the cleaned gas.

Table 1 Results from analyses of NDELA, nitrosodimethylamine (NDMA) and DEA in MEA solvent samples.

| Experiment no. | Process variables O2 vol% | Process variables NOx ppmv | NDELA Absorber end sample (ng/g) | NDELA Autoclave end sample (ng/g) | NDMA Autoclave end sample (ng/g) | DEA Absorber end sample (µg/g) | DEA Autoclave end sample (µg/g) |
|---|---|---|---|---|---|---|---|
| A09-0084 | 14 | 25 | 420 | - | - | - | - |
| A09-0090 | 14 | 25 | 320 | - | - | - | - |
| A09-0180 | 7 | 25 | 146 | 6515 | 4 | 30.5 | 360.3 |
| A09-0188 | 0 | 45 | 509 | 2178 | 4 | 33.3 | 214.8 |
| A09-0209 | 7 | 25 | 261 | 6643 | 4 | 27.5 | 369.4 |
| A10-0001 | 0 | 5 | 23 | 85 | <1 | 12.8 | 35.6 |
| A10-0004 | 7 | 25 | 133 | 4711 | 2 | 24.4 | 245.2 |
| A10-0010 | 7 | 5 | 22 | 670 | <1 | 28.9 | 102.9 |
| A10-0014 | 7 | 45 | 716 | 25641 | 5 | 50.5 | 612.1 |
| A10-0017 | 0 | 25 | 130 | 1247 | <1 | 23.2 | 131.1 |

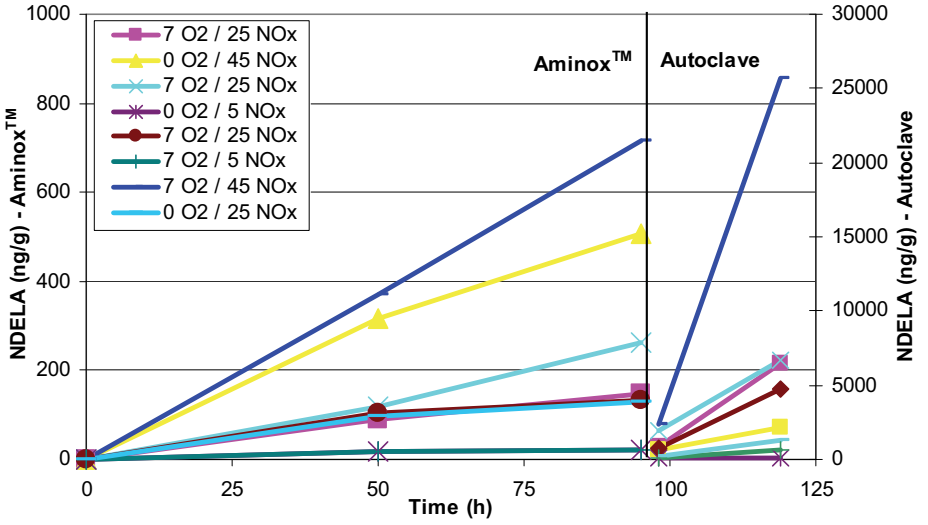



Figure 2 Formation of NDELA in MEA solvent during Aminox™ and autoclave testing. (Key to legend: 7 O2 / 25 NOx denotes experiment with 7 vol% O2 and 25 ppmv NOx).

The secondary amine, diethanolamine (DEA) is likely to be the precursor for NDELA. DEA may be present as an impurity in MEA, but may also be formed as a degradation product. The concentration of DEA in fresh 35 w% MEA solvent was 10 µg/g and the concentration increased during degradation of the MEA solvent as illustrated in Figure 3. The formation rate of DEA was speeded up at high temperature in the autoclave. The profile is similar to

the NDELA formation profile and this supports the idea that DEA is the NDELA precursor. The concentration of DEA in end samples from absorber degradation was in the range 10-50 µg/g and about 10 times higher after exposure to high temperature.

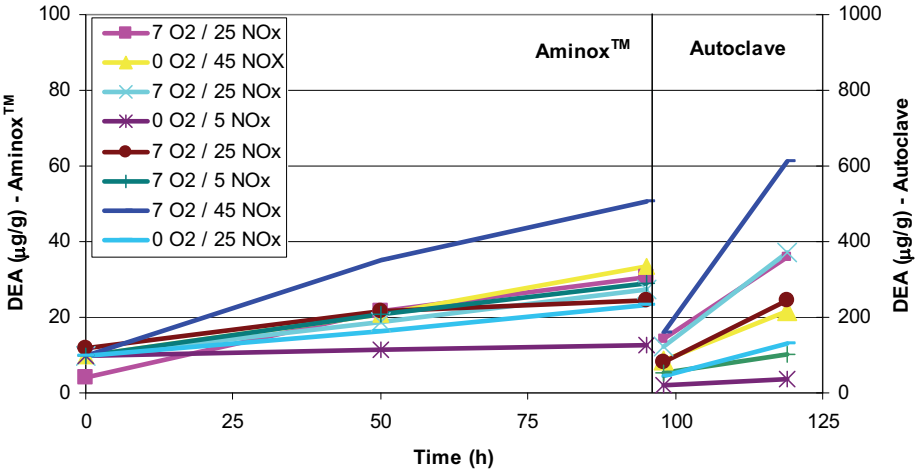



Figure 3 Formation of DEA in MEA solvent during Aminox™ and autoclave testing. (Key to legend: 7 O2 / 25 NOx denotes experiment with 7 vol% O2 and 25 ppmv NOx).

A multivariate data analysis tool Simca-P+ was used to establish a regression model for prediction of NDELA formation in MEA solvent at Aminox™ absorber conditions. The model was based on the process variables $O_2$ and NOx and the main chemical response variables measured. The model has high correlation coefficients and acceptable prediction precision. In Figure 4 plotted lines represent predicted NDELA levels at 100 hours Aminox™ testing, for two levels of oxygen and varied NOx concentrations. Points illustrate measured values. The formation rate of NDELA increases along with the NOx concentration of the gas, and to some extent also with the oxygen level. Even at very low NOx concentrations (5 ppmv), nitrosation of MEA was observed.

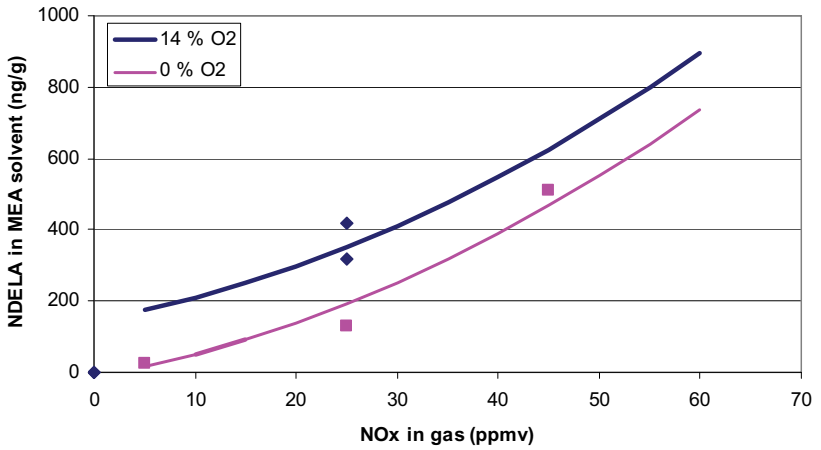



Figure 4 Predicted (solid lines) and observed (symbols) NDELA concentrations in MEA solvent at Aminox™ absorber conditions.

Primary amines like MEA give highly unstable nitrosamines in reactions with nitrosating agents [13]. The deamination mechanism of primary amines shown in Figure 5 goes via an unstable diazonium ion intermediate which can react with nucleophiles to give various substitution, elimination and rearrangement products.

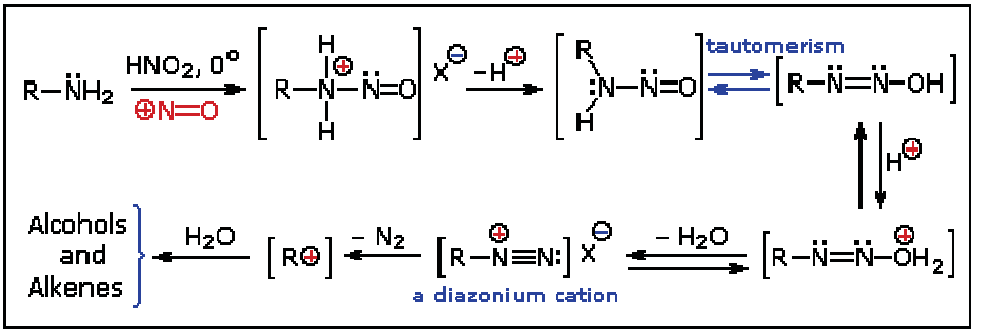



Figure 5 Deamination mechanism of primary amines. (Source: Virtual textbook of organic chemistry).

One out of several competing reactions is the formation of a secondary amine $R_2NH$:

$$R\text{-}N{\equiv}N^{+} + RNH_2 \rightarrow R_2NH + N_2 + H^{+} \quad (1)$$

This reaction pathway is favoured by high amine concentration, which indeed is the case in the process. It is of the same reason less likely to play a role in the water wash section and in the atmospheric reactions post emission. The secondary amine formed can be nitrosated to a stable nitrosamine according to the mechanism illustrated in Figure 6.

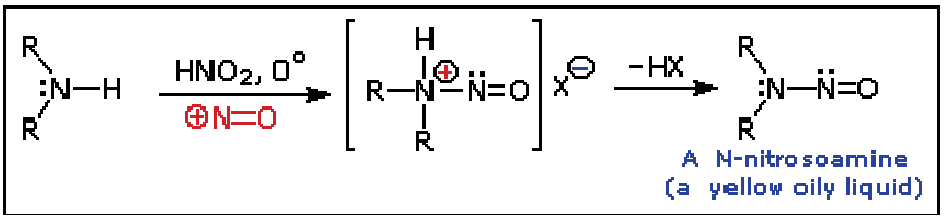



Figure 6 Nitrosation of a secondary amine. (Source: Virtual textbook of organic chemistry).

These reaction schemes can explain the formation of NDELA via DEA as found in this work.

*3.2. Formation of other nitrosamines, nitramines and alkylamines*

In addition to NDELA, also traces of nitrosodimethylamine (NDMA) were detected in used solvent samples that had been heated in the autoclave. The concentration of NDMA was in the 5 ng/g range as shown in Table 1.

The online-FT-IR analyzer indicated a MEA slip of 100 ppmv from the absorber. This was reduced to below 1 ppmv in the water wash step. No nitrosamines were detected in the gas. However, the FT-IR instrument was not sensitive enough to detect very low concentrations of these compounds. An online-MS system with the capability of detecting components in low ppb to ppt area was thus tested. The MS-instrument was connected to the Aminox$^{TM}$ gas sampling lines for some days and then to the autoclave gas phase. A significant signal of a mass identical to the mass of NDMA was detected in the absorber off gas. A qualitative control was performed by analysis of a multi standard of known nitrosamines including NDMA. By analysis of the autoclave gas phase during heating of the used solvent, significant signals of NDMA, nitrosomorpholine (NMOR) and masses corresponding to some other

nitrosamines in the multi standard were detected. The compounds were identified as trace elements in the gas, no quantification was done.

NDMA and NMOR are volatile nitrosamines that may be formed from nitrosation of the corresponding amines morpholine (MOR) and dimethylamine (DMA), or by degradation of NDELA which builds up in the solvent over time [17]. A hypothetic reaction scheme that presents possible amine and nitrosamine formation pathways from MEA is illustrated in Figure 7. The reaction scheme is simplified, intermediate amines may form. Underlined compounds in red can directly form stable nitrosamines. Only nitrosamines observed experimentally are included in the scheme. NMOR has not been detected in liquid samples, only as trace compound in autoclave gas samples.

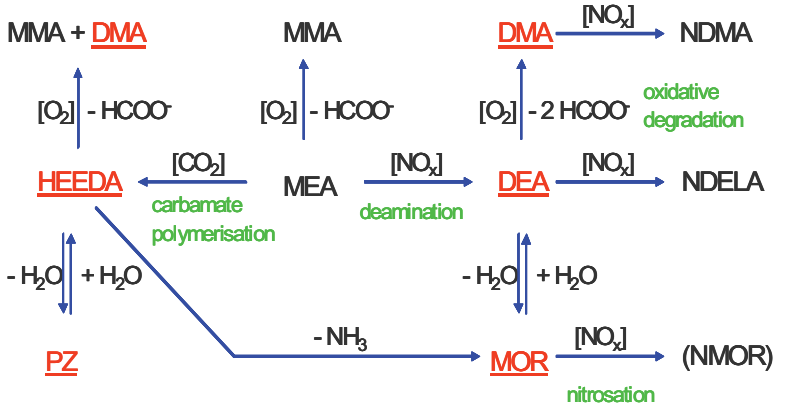



Figure 7 Proposed formation pathways of amines and nitrosamines from degradation of MEA. HEEDA and PZ denote N-(2-hydroxyethyl)-ethylenediamine and piperazine, respectively.

The small and volatile alkylamines, monomethylamine (MMA) and dimethylamine (DMA) are also possible degradation products from MEA [7, 10]. These are especially important since they may form nitrosamines and nitramines in the atmosphere post emission [4-6]. Due to their volatility these compounds will tend to escape with the cleaned gas. MMA and DMA have not been detected in solvent or wash water samples. Traces of MMA in absorber off gas were significantly detected by the FT-IR at the end of the experiment with highest NOx. MS detection of MMA and DMA was not possible due to interferences with other masses.

Nitramines have not been detected in MEA solvent samples. However, the detection limits were high (100 μg/g), better analytical methods are thus needed to evaluate nitramine formation in the process.

## 4. Evaluation of the experimental setup

The experimental set-up using the Aminox™ test rig for studying flue gas degradation and further exposing the degraded solvent to higher temperature in a laboratory autoclave has proven to be a good method to identify important degradation by-products from MEA. However, it has a few limitations. The autoclave is not integrated in the test rig so the effect of circulating the regenerated solvent back to the absorber has not been evaluated. One expected effect is that the carbamate polymerisation products that form at higher temperatures and may give rise to alkylamines are in very low concentrations in the Aminox experiments. Alkylamines are therefore possibly underestimated. The experimental setup should thus primarily play the role of identifying the compounds that need to be measured in a pilot plant.

The development of analytical methods for quantification of harmful degradation by-products from MEA has run in parallel with the experimental testing. Sensitive methods for analysis of nitrosamines in solvent samples based on LC-MS have been established. More work still needs to be done on analysis of nitramines and on gas sampling and analysis of volatile nitrosamines and alkylamines.

## 5. Conclusions

The health and environmental impact of emissions to air from amine based $CO_2$ capture is a remaining risk that needs to be clarified. In this work, the flue gas degradation of MEA in the process has been studied with special focus on NOx induced chemical reactions and formation of potential harmful compounds.

MEA is a primary amine and therefore among the amines with the lowest potential to form nitrosamines. However, this work has shown that MEA degrades to the secondary amine DEA under influence of NOx. DEA is then nitrosated to NDELA, which was the main nitrosamine observed. NDELA is fortunately non-volatile but traces of two volatile nitrosamines, NDMA and NMOR have also been detected. The volatile alkylamines MMA and DMA which may form nitrosamines and nitramines in the atmosphere post emission, were challenging to analyse due to interferences and instrument sensitivity. Hence, the importance of nitramines and alkylamines should be examined further.

This work shows that some nitrosamine formation in the process must be expected from any amine. Based on data from real emission measurements, health and environmental risk assessment should be investigated in further studies.

## Acknowledgements

Statoil wish to acknowledge the Climit program of the Research Council of Norway for financial support to the Flue gas Degradation of Amines (FDA) project. Statoil also thanks SINTEF and Tel-Tek for important contributions to the project and colleagues Ingvar Eide and Gunhild Neverdal who have performed the multivariate data analysis.

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